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Article

One-Pot, High-Yield Synthesis of Size-Controlled Gold Particles with Narrow Size Distribution

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Here, we first report a facile one-step one-phase synthetic route to achieve size-controlled gold micro/nanoparticles with narrow size distribution by using *o*-diaminobenzene as a reducing agent in the presence of poly(*N*-vinyl-2-pyrrolidone) via a simple wet-chemical approach. All experimental data including that from scanning-electron microscopy, energy-dispersive X-ray spectroscopy, X-ray photoelectron spectroscopy, and X-ray diffraction techniques indicates that the gold micro/nanoparticles with a narrow size distribution were produced in high yield (∼100%).

Introduction

The development of nanoparticles has been intensively pursued, not only for fundamental scientific interests but also for many potential technological applications. Gold nanoparticles, especially, hold promise for uses as advanced materials with novel optical, electronic, thermal, and catalytic properties due to their potential applications in several fields of catalysis, biological labeling, and sensing,[1−5] and thus the synthesis and characterization of gold nanoparticles have attracted considerable attention from a fundamental and practical point of view.[6] To date, some protective agents such as surfactants,[7] polymers,[8,9] thiols,[10,11] dendrimers,[12] and ionic liquids[13] have been employed to prepare the spherical gold nanoparticles in both organic and aqueous media. For instance, Wang et al.[12] have developed a heat-treatment-based strategy for the one-step preparation of dendrimer-protected gold nanoparticles with the use of an amine-functionalized third-generation poly(propyleneimine) dendrimer to simultaneously act as both the reducing agent and protective agent. The synthesis and functions of gold nanoparticles modified with ionic liquids based on the imidazolium cation were well-developed by Naka's group.[13] However, in general, gold nanoparticles reported in the literature were small and polydisperse, and in the meantime, it is difficult to adjust the diameter of gold nanoparticles in the wider range. Recently, several studies[14] have reported the synthesis of quasi-monodisperse gold micro/nanoparticles through different approaches in the aqueous or organic phase. For instance, Kuhn et al.[14a] reported a straightforward method to synthesize quasi-monodisperse gold microspheres via decomposing and precipitating $[\mathrm{Au(SO_3)_2}]^{3-}$ under acidic conditions. Klabunde's group[14b] demonstrated a synthetic procedure for the preparation of large quantities of quasi-monodisperse thiol-stabilized gold colloids in toluene solution. However, there has only been limited success in the synthesis of gold micro/nanoparticles with the controllable size ranging from 150 nm to 1 μm despite the fact that these colloidal gold micro/nanoparticles may also find important

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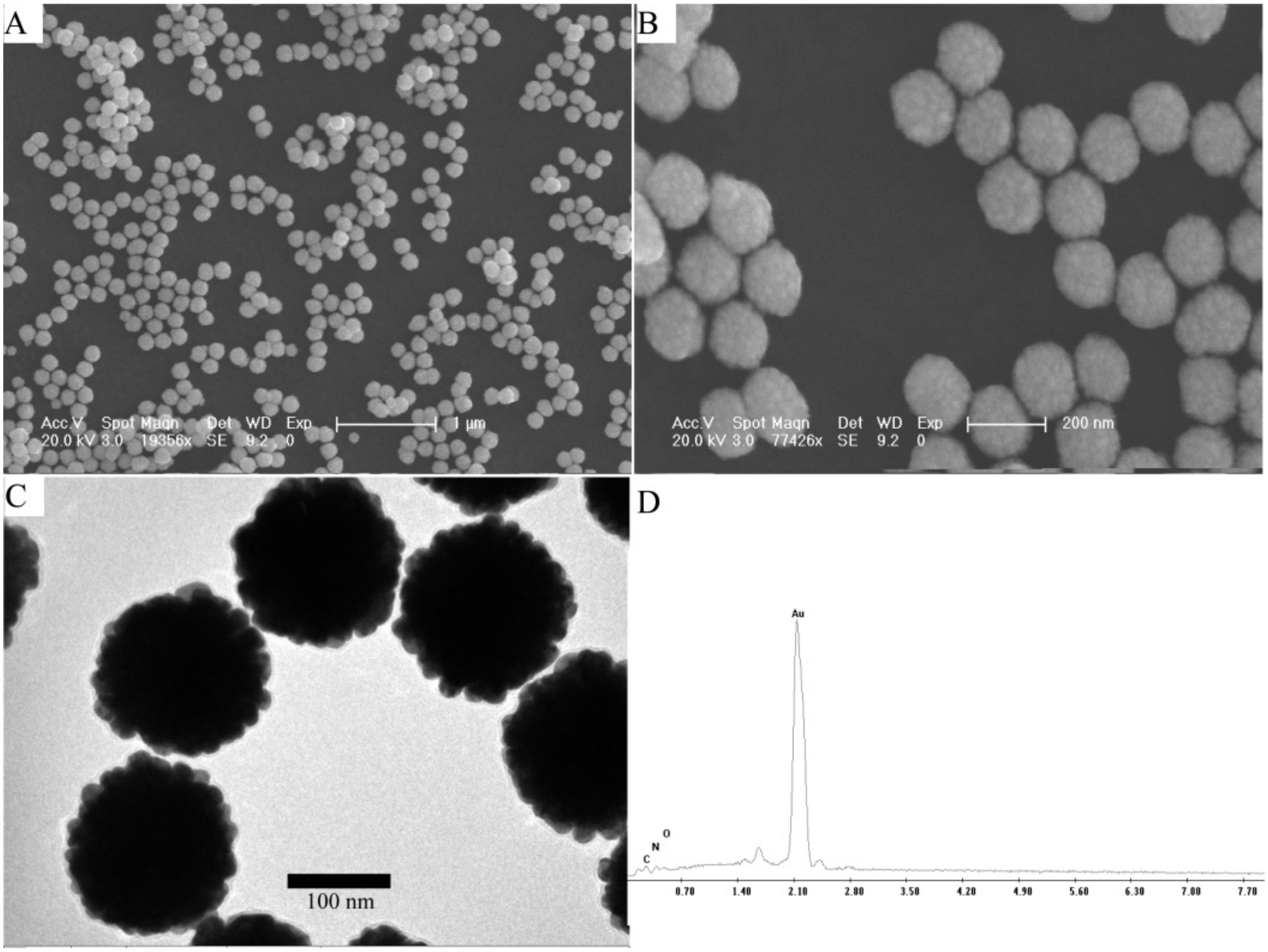

Figure 1. Typical FE-SEM images of sample 1 (PVP to gold ratio of 30:1) located at Al foil substrate at low-magnification (A); and high-magnification (B). Typical TEM image of sample 1 (C); the EDX image of sample 1 (D).

applications in catalysis, surface-enhanced Raman spectroscopy (SERS), sensing, electronics, and photonics. So it is necessary to introduce a simple, novel, and rapid route to the synthesis of size-controlled gold micro/nanoparticles with narrow size distribution. Here, we report a facile one-step one-phase synthetic route to achieve size-controlled gold micro/nanoparticles with a narrow size distribution by using *o*-diaminobenzene (*o*-DAB) as a reducing agent (a moderate reducting agent with high solubility in water) in the presence of poly(*N*-vinyl-2-pyrrolidone) (PVP) via a simple wet-chemical approach. In this synthesis system, PVP was used as the capping agent, which controlled the growth of the particle and stabilized the micro/nanoparticles after they formed. The gold micro/nanoparticles with narrow size distribution were produced in high yield (∼100%).

Experimental Section

Chemicals. $HAuCl_4 \cdot 4H_2O$, PVP, and *o*-DAB were all purchased from Beijing Chemical Factory (Beijing, China) and used as received without further purification. All aqueous solutions were prepared with ultrapure water (Millipore system). Three samples were prepared according to the following procedure: First, 2 mL of 25 mM $HAuCl_4$ aqueous solution and 0.1 M PVP aqueous solution with the initial molar ratios of 30:1, 5:1, and 1:1 of PVP to gold (corresponding to samples 1, 2, and 3, respectively) were placed in a small beaker. The resulting solution was diluted to a 7.5 mL volume with water, and then 0.5 mL of 0.1 M *o*-DAB aqueous solution was added. After stirring for several hours at room temperature, the solution was centrifuged for three times in water and ethanol, respectively.

Apparatus. Transmission electron microscopy (TEM) measurements were made on a JEOL 2000 transmission electron microscope operated at an accelerating voltage of 200 kV. Samples for TEM characterization were prepared by placing a drop of sample onto a carbon-coated copper grid and then drying at room temperature. X-ray diffraction (XRD) analysis was carried out on a D/Max 2500 V/PC X-ray diffractometer using Cu (40 kV, 30 mA) radiation. Analysis of the X-ray photoelectron spectra (XPS) was performed on an ESCLAB MKII using Mg as the exciting source. Scanning-electron microscopy images were determined with a Philips XL-30 ESEM. The accelerating voltage was 15 kV.

Results and Discussion

Parts A and B of Figure 1 show the typical SEM images of the as-prepared sample 1 coated on the Al foil substrate. As shown, the Al substrate is covered with a great deal of gold spheres with a narrow size distribution. Figure 1C shows

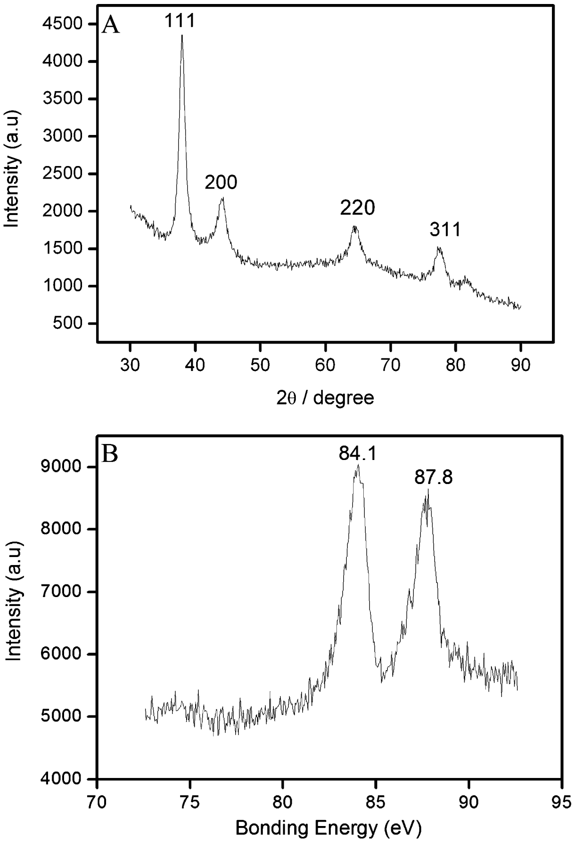

Figure 2. XRD (A) and XPS pattern (B) of sample 1 (PVP to gold ratio of 30:1) located at glass slide.

the TEM image corresponding to sample 1. Unusual submicrometer spheres with a size of about 150 nm (standard deviation <5%), which are composed of small nanoparticles with diameters of about 10 nm, were observed. Note that the gaps between the gold submicrometer spheres are less than 10 nm, which was reported to be favorable for the production of a strong electron magnetic field for the SERS effect.[15] Thus, the as-prepared gold submicrometer spheres will find potential applications in SERS.

The chemical composition of gold submicrometer spheres was determined by energy-dispersive X-ray spectroscopy (EDX). The EDX spectrum (Figure 1D) with only one main peak corresponding to Au (two low-intensity peaks around the main gold peak originated from Au, which were caused by different energy-level differences of the gold atom), revealed that these gold submicrometer spheres were pure metallic Au. The unique gold spheres were further characterized to determine their crystal direction. XRD measurement has confirmed that the as-prepared sample 1 is gold crystals with face-centered cubic lattice structure, as shown in Figure 2A. The peaks located at 37.9°, 44.3°, 64.3°, and 77.2° were assigned to (111), (200), (220), and (311) facets of gold submicrometer spheres, respectively. The intensity ratio of the {111} to the {200} diffraction line is higher than the 1.9 value of the standard diffraction of gold powders, indicating that the deposited gold structure has the tendency to grow with the surfaces terminated by the lowest energy {111} facets.[16] To further confirm the formation of metallic Au, XPS was used to identify the change in oxidation states for Au after the reaction had occurred. Figure 2B shows the XPS spectrum of the resulting sample 1. It was found that the Au 4$f_{7/2}$ peak appears at a binding energy of 84.1 eV, and the Au 4$f_{5/2}$ peak appears at a binding energy of 87.8 eV. These observations clearly confirm the formation of metallic gold after the reaction.[17]

It was observed that the size and morphology of the gold crystals obtained in the presence of PVP were significantly influenced by the molar ratio of PVP to $HAuCl_4$. As shown in parts A and B of Figure 3, the quasi-monodisperse gold submicrometer spheres with diameters of about 500 nm were formed when the molar ratio of PVP to $HAuCl_4$ decreased to 5:1. Local magnification (Figure 3B) shows that these gold submicrospheres with narrow size distribution (standard deviation <10%) are rough on the nanoscale. If the PVP concentration was further decreased (sample 3), the quasi-monodisperse microspheres with diameters of 1 μm (standard deviation <10%) were generated. Figure 3C shows the TEM image corresponding to sample 3, which clearly indicates the gold microspheres own narrow size distribution. Corresponding local magnification of TEM (Figure 3D) shows that the surface of the microspheres is nearly smooth. As mentioned above, since PVP was a vital additive, adjusting the morphology of the resulting products, if no PVP was used in the solution, the micro/nanospheres with a narrow size distribution would disappear, leading to irregular nanoparticle aggregates, as shown in Figure 4.

On the basis of the above data and literature,[14c] a possible formation mechanism of micro/nanospheres was initially proposed. Matijević et al. proposed the formation mechanism of gold nanoparticles characteristic of smooth and rough surfaces. That is, when the primary (nanosize) particles are formed, the subsequent diffusion of gold atoms onto them may continue (leading to particles with smooth surfaces) or they can aggregate to form the final big gold particles with rough surfaces. In our system, the reduction of $HAuCl_4$ using *o*-DAB as the reductant initially produced primary gold particles. Then, PVP was adsorbed on the surface of gold.[18] If the concentration of PVP was low, the subsequent formation of the gold atom, which was produced via a reduction of $HAuCl_4$, was diffused into the primary gold particles and the quasi-monodisperse gold microsphere with a near-smooth surface was obtained. However, when the concentration of PVP was high, the primary gold nanoparticle would probably grow, and also, excess PVP induced the aggregation of small nanoparticles until equilibrium between them was reached. Finally, submicrospheres consisting of many nanoparticles aggregates were obtained. However, the detailed formation mechanism of the micronanospheres in

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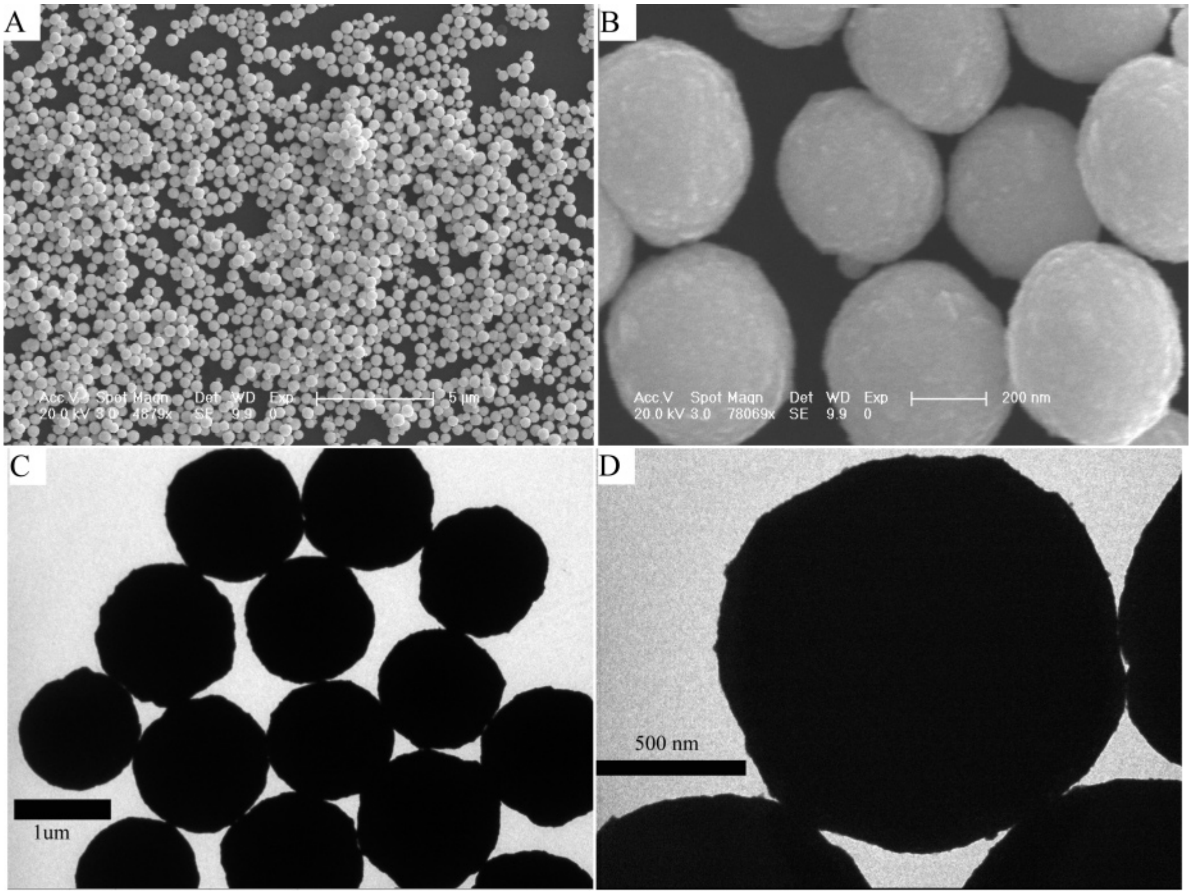

Figure 3. Typical SEM images of sample 2 (PVP to gold ratio of 5:1) at low magnification (A); and high magnification (B). Typical TEM images of sample 3 (PVP to gold ratio of1:1) at low magnification (C); and high magnification (D).

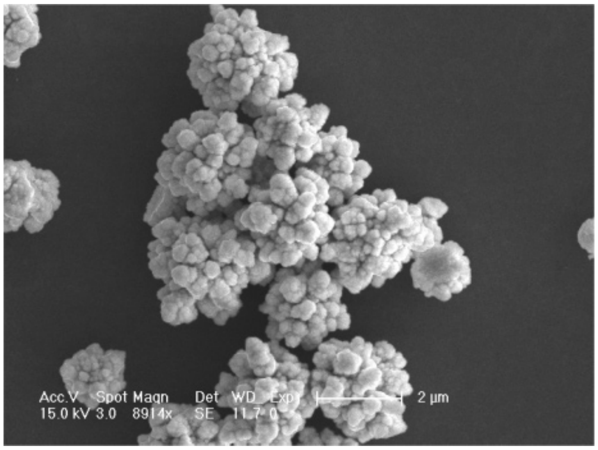

Figure 4. Typical SEM image of the sample without the addition of PVP.

this synthesis is not very clear at the present time and needs further study.

Conclusion

In conclusion, we have demonstrated that gold micro/nanoparticles with narrow size distribution can be prepared via a simple wet-chemical approach in aqueous solution at room temperature. The diameter of the gold micro/nanoparticles can be easily controlled via changing the molar ratio of PVP to $HAuCl_4$. Our observations are significant for the following reasons. First, the study is of significance for controlling the monodisperse size and uniform shape of nanoparticles, which is essential for achieving applications in the biomedical and sensor fields. Second, this simple one-pot synthetic method can be extended to make micro/nanoparticles of Ag and other metal alloys with new structures.

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